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THEORETICAL MODELLING OF CELL AND BATTERY CHARACTERISTICS AT SHORT TIMES/HIGH FREQUENCIES

By

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INTRODUCTION :

The design of batteries intended to deliver very high current pulses with rise times on the order of microseconds requires consideration of factors usually neglected in conventional battery design. In previous work [1] we have shown that the short time/high frequency response of a physically large battery may be significantly limited by geometric and physical factors. In constructing theoretical models which can be used to evaluate design factors in pulse batteries it is therefore necessary to take into account the whole battery, including the plate geometry, the internal and external connections, and eventually the load itself. On the basis of a modelling study which takes some of these factors into consideration, this paper describes the design implications of geometric and physical variables such as electrode and electrolyte resistivity, electrolyte thickness, and cell length.

The details of the modelling procedure are described elsewhere [1,2], and are only summarised here. The results described in this paper have been obtained for a single cell of semi-infinite rectangular parallel-plate geometry (a stripline cell) with infinitely thick solid electrodes (Figure 1). The assumption of infinite electrode thickness does not affect the results at the high frequencies of greatest interest since nearly all the current is carried at the surface of the conductor, but will lead to errors at low frequencies. The modelling has been carried out by considering the cell behavior as that of a distributed network comprised of differential elements having the equivalent circuit shown also in Figure 1. The series components are the electrode inductance, L_s, and the skin effect resistance, r_{sk}. The parallel components comprise three series combinations of a resistor in parallel with a capacitor. These represent the positive electrode interface (subscript W), the electrolyte (subscript E), and the negative electrode interface, (subscript C), respectively. The values of L_s, r_{sk} and the electrolyte components can be estimated from the physical and geometric properties of the cell as described elsewhere [1]. For the calculations reported here the value of the

Faradaic resistance of the negative electrode has been assumed infinite, so that this electrode behaves as a bare metal showing capacitative behavior only. On the basis of this equivalent circuit the impedance of the cell has been calculated over a wide range of frequencies from 10^2 to 10^8 Hz. By use of inverse Fourier transformations it has also been possible to calculate the transient response of the cell, for example the transient voltage response to a current pulse of unit amplitude.

RESULTS AND DISCUSSION :

The effects of a number of the design variables on the cell characteristics have been calculated using the approach described above. The variables studied include electrode and electrolyte resistivity, electrolyte thickness, interfacial resistances and capacitances, and cell length.

Fig 2, which has been taken from [1], illustrates a number of the different types of limiting behavior that can be calculated. The results are presented as Bode plots for log Z (the modulus of the complex impedance), and the phase angle theta. A set of plots is given for electrolyte resistivities ranging from 10^{-2} to 10^3 Ω.cm. Over limited frequency ranges, the behavior can be described by simplified versions of the equivalent circuit given in Fig. 1. The illustrations of this given at the top of Fig. 2 correspond to the case where the electrolyte resistivity is 10^2 Ω.cm. For this particular curve, it can be seen that at high frequencies (region E) the cell impedance is dominated by the series inductance of the electrodes and the parallel capacitance of the electrolyte. (Note that no interfacial components contribute). LC network behavior is seen and the impedance has the characteristics of a pure resistor (log Z constant and a phase angle of zero). As the frequency decreases (region D), r_E becomes less than $1/\omega C_E$ and the behavior becomes that of an LR circuit. As the frequency continues to decrease ωL_s becomes comparable to r_{sk} (region C), and once r_{sk} becomes the dominant series component the behavior becomes purely resistive. At the lowest frequencies shown (region A) the interfacial capacitance C_{dl} becomes the dominant parallel term and the behavior becomes that of an RC network.

Also shown in Fig. 2 is the dependence of the penetration length 1/alpha on frequency. For a given frequency, all but 1/e of the total current is drawn from a distance of 1/alpha from the terminals [1]. The penetration length therefore gives a measure of the fraction of the cell that can be utilised at a particular frequency. As Fig. 2 shows, penetration decreases at higher frequencies/shorter times. Over the frequency range shown, increasing the electrolyte resistivity leads to an increase in the penetration length.

Figure 3 shows the effect of the Faradaic impedance of the positive electrode, r_F, on the impedance of an infinite line. Low values of r_F have the greatest effect, acting to short out C_W and thereby reduce the overall impedance at intermediate frequencies to the value determined by the other parallel components. At very high frequencies r_E and L_s dominate and RL line behavior is seen, while at low frequencies r_E and C_C dominate and the behavior is that of a RC line. The frequency at which the effect of r_W shorting out C_W appears increases as the value of r_E decreases.

Figure 4 shows the results of the same calculations but in the form of the voltage transient response to a current step of unit amplitude. The method by which the conversion from frequency to time domain is carried out is described elsewhere [2]. At short times the cell behavior is primarily inductive and the voltage decreases rapidly. For very low values of Faradaic resistance the cell behavior then becomes resistive and the voltage becomes constant with time. Beyond a few hundred microseconds in the low r_F case the cell becomes inductive again (voltage decreasing with time) and this can also be seen, although less clearly, in the corresponding curves in the frequency domain in Fig. 3. At longer times still, though, the cell becomes resistive, and then finally shows capacitative behavior as C_W becomes dominant. Similar progressions in characteristic behavior with time can be seen with the higher values of r_F, but displaced to longer times. Thus for r_F greater than 10^{-1} Ohms the behavior is still inductive after a millisecond.

The previous examples have treated cases where the cell is infinitely long. This corresponds in practical terms to situations where the physical dimensions of the cell exceed about three times the penetration length at the frequencies considered. Figure 5 illustrates in Bode plot form the case where the cell is of finite length, that is where the pulse has time to penetrate to the end of the cell. At high frequencies (corresponding to periods too short for the pulse to reach the end of the cell) the behavior is identical to that of the infinitely long line. At low frequencies the cell behavior approaches that of a pure capacitor; the impedance becomes inversely proportional to frequency. This corresponds to the discharge of the cell in the conventional manner. In the intermediate frequency region where the length of the cell is of the same order as the penetration length, oscillatory behavior in both the magnitude of the impedance and the phase angle is seen, and this is believed to result from constructive and destructive interference as the pulse is reflected from the end of the cell. The frequency at which the finite length of the cell affects the output increases as expected as the length of the cell decreases. For practical purposes it is desirable to construct a cell that is just long enough to behave as if it were infinitely long at the output frequency/pulse length required. Any extra capacity does not contribute to the performance of the cell and therefore reduces the overall efficiency.

The modelling approach illustrated here permits quantitative calculation of the performance of a pulse battery at high frequencies/short times where many intuitive concepts derived from an understanding of steady-state behavior do not apply. It is not possible to list here all the calculated effects of the design variables that have been studied, but Table 1 illustrates, for a particular set of conditions, the way in which design factors can influence the characteristics of the cell. Many of these effects, particularly on the penetration length, would be difficult to predict intutitively, and a factor that would have a significant effect on performance at one frequency may have no effect at another.

SUMMARY :

The effect of a number of design variables on the performance of cells at short times/high frequencies has been calculated by modelling the cell as a distributed network. For a stripline geometry, it has been possible to calculate that at sufficiently short discharge times the performance of the cell is limited by physical and geometric effects, independent of the electrochemistry. It has also been shown that for a desired output frequency/pulse length, there is an optimum size of cell, and that scaling up beyond this size produces no improvement in performance.

ACKNOWLEDGEMENT : This research has been supported by ONR through a subcontract with Eveready Battery Co.

REFERENCES

1. B.D. Cahan, M.L. Daroux, E.B. Yeager ; Impedance of Electrochemical Power Sources I. Physical and Geometric Effects, 171st Electrochemical Soc. Meeting Extended Abstracts 87-1, Philadelphia, May 1987 (submitted to J. Electrochem. Soc.)

2. M. L. Daroux, B.D. Cahan, J.P. Discenza, E.B. Yeager ; Modelling Studies of the Short Time/High Frequency Behavior of Pulse Batteries (in preparation)

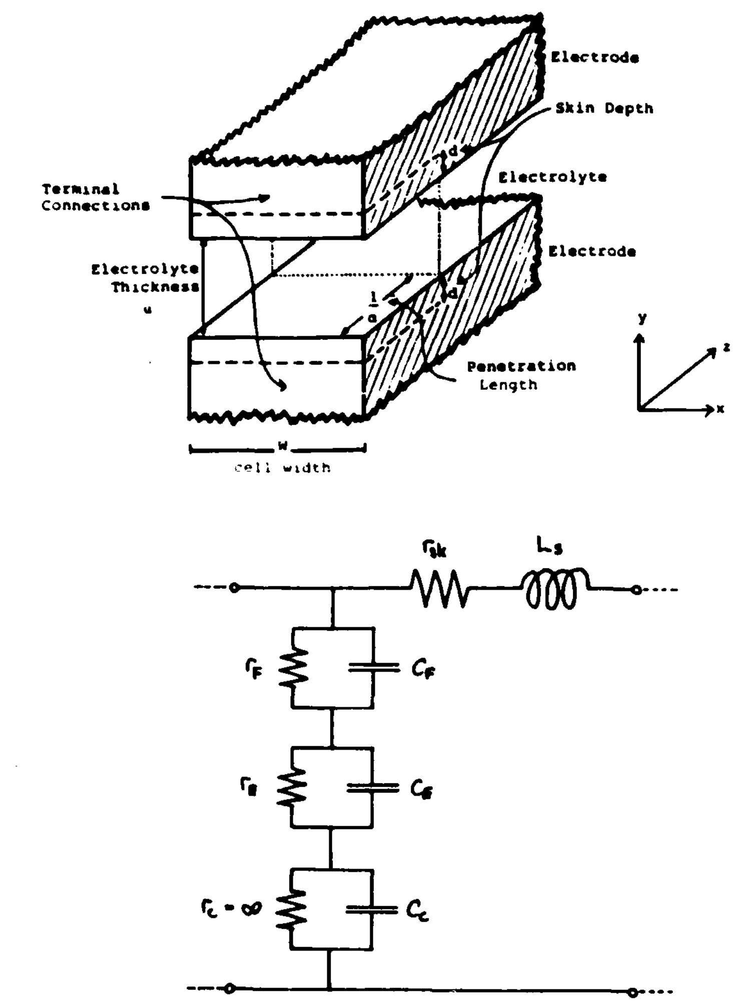

FIGURE 1 : Geometric Model of a Semi-infinite Rectangular Parallel Plate (Stripline) Cell, together with the corresponding Equivalent Circuit Representation of the Physical and Electrochemical Components.

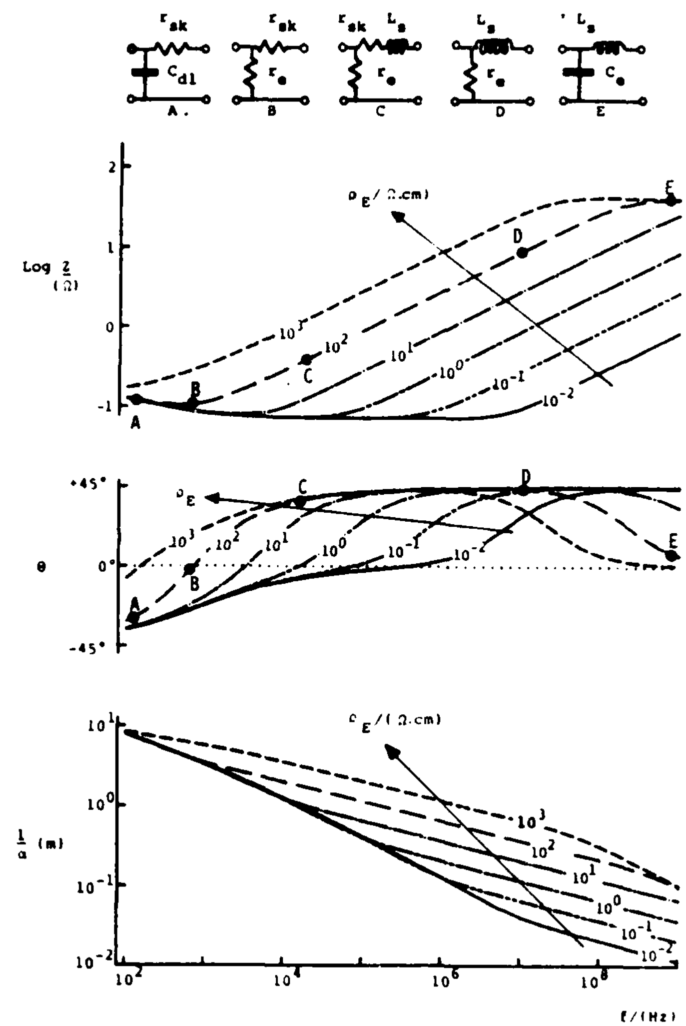

FIGURE 2 : Bode Plots showing the Effect of Electrolyte Resistivity ρ_E for ρ_M (electrode resistivity) = 3.5×10^{-3} Ω·cm, ρ_E = 10^{-2} - 10^{3} Ω·cm, u (electrode spacing) = 0.1 cm, W = 1.0 cm, C_F, C_C = 50 μF/cm², C_E = 7.17×10^{-5} μF/cm², L_s (electrode inductance) = 1.255×10^{-9} H/m, r_F, r_C infinite

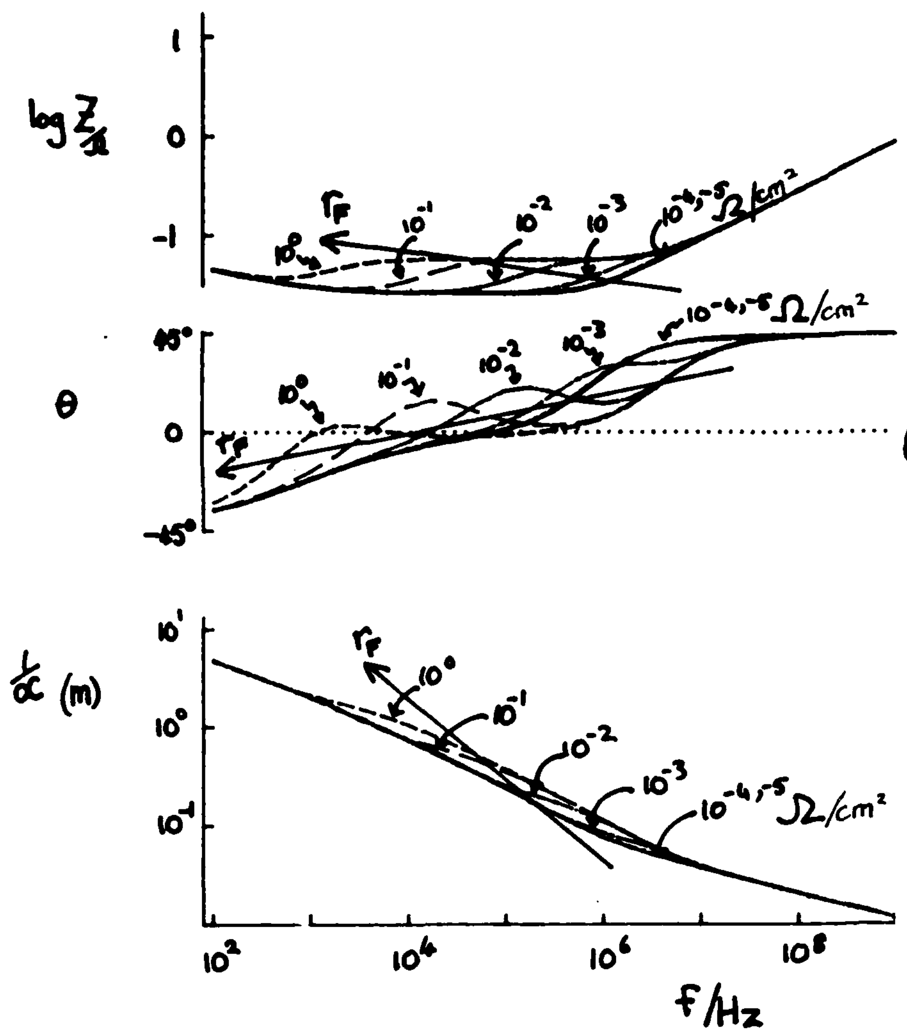

FIGURE 3 : Bode Plots showing the Effect of Faradaic Resistance. Conditions are the same as for Fig. 2 except that $\rho_E = 10^{-2}$ Ω-cm, C_C = 200 μF/cm², and $r_F = 10^{-5} - 10^{0}$ Ω/cm².

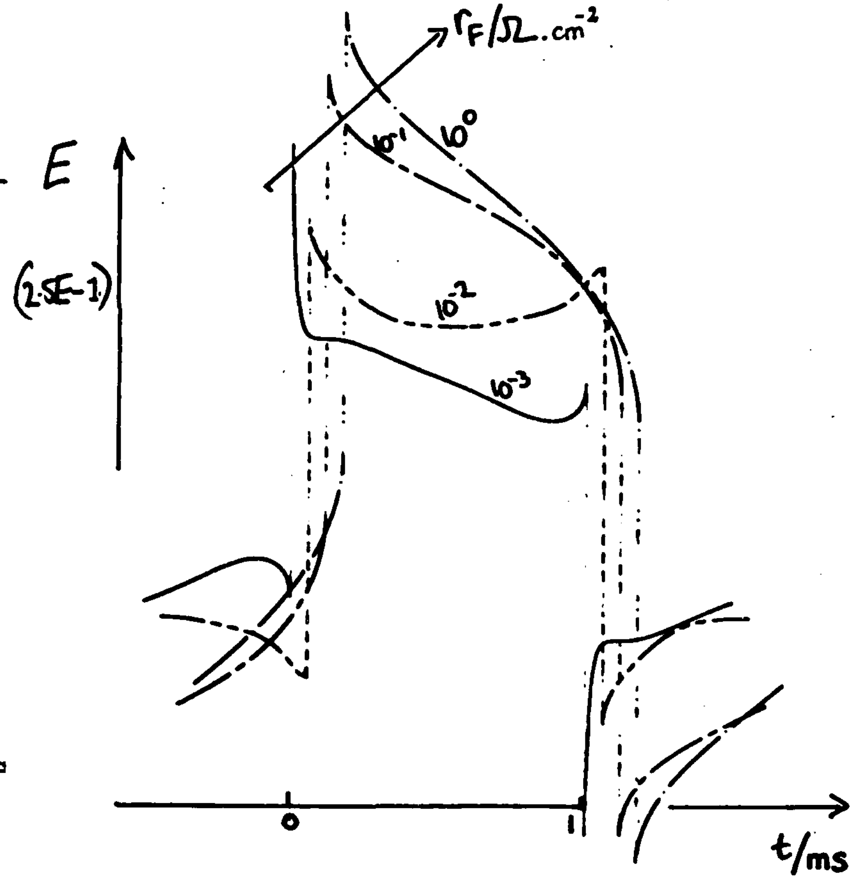

FIGURE 4 : Voltage Transient Response to a Unit Current Step, showing the Effect of Faradaic Resistance. Conditions are identical to those for Fig. 3.

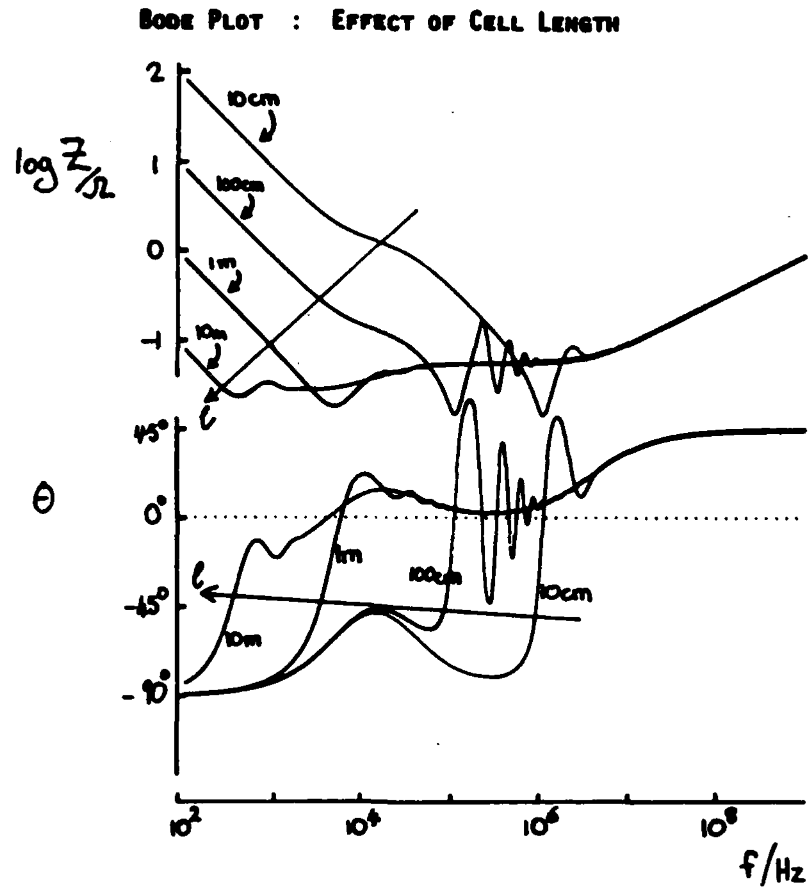

FIGURE 5 : Bode Plots showing the Effect of Cell Length. Conditions are the same as for Fig. 3 except that $r_F = 10^{-3}\ \Omega/cm^2$.

TABLE 1 : Summary of the Effects of the Variables considered on the Characteristics of a Stripline Cell. Applicable to the conditions given for Figure 3. The trends listed correspond to an increase in the value of the variables.

VARIABLE	IMPEDANCE		PENETRATION LENGTH
	10^3 Hz	10^6 Hz	
ELECTRODE RESISTIVITY	increased	unaffected	decreased
ELECTROLYTE RESISTIVITY	increased	increased	increased
ELECTROLYTE THICKNESS	slightly increased	increased	decreased
CELL LENGTH (FINITE)	decreased	little to no effect	increased
INTERFACIAL RESISTANCE	increased	unaffected	increased
INTERFACIAL CAPACITANCE	decreased	decreased slightly	decreased